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# Constant-NT $\mu$ Simulations: Free Energy Difference Method for Excess Adsorption

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## ABSTRACT

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We describe a new method to simulate confined fluids in equilibrium with a bulk. The equilibrium is first located at a low density, where conventional methods relying upon real or virtual particle exchanges are reliable. Thereafter, the chemical potential of the fluid is increased by the same amount in both systems using a variation of a recently developed free energy difference method in an isobaric (isotension) ensemble. The method, illustrated here for a simple fluid in a planar slit, is shown to be reliable up to high densities. As the method does not rely upon particle exchanges it is ideally suited to the simulation of equilibria in complex fluids, e.g., molecular liquids and polymers. © 1996 by John Wiley & Sons, Inc.

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## Introduction

**T**he study of nonuniform and confined fluids has been of interest for decades. For example, it finds application when considering the stability of colloids<sup>1,2</sup> and in studies of catalysis and membrane separation.<sup>3</sup> One area that has occupied our interest for some time, has been the study of solvation forces between surfaces at short separation.<sup>4</sup> These forces are of vital importance in determining the stability of dispersions and other types of macromolecular solutions. Apart from the fundamental scientific considerations, there are obvious

commercial benefits to understanding the properties of such systems.

Many different approaches have been used in the theoretical studies of confined fluids. These include computer simulations, integral equations, and density functional theory. Of these, computer simulations have the important advantage of providing exact answers for a given model system. In contrast, the other theoretical methods invariably involve approximations. Indeed their limitations and suitability for a particular application are often assessed by simulations.

Only relatively few simulations, addressing equilibria between a confined fluid and a bulk reservoir, have been reported. This has limited our understanding of confined fluids, but is easy to

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understand when the available techniques for simulating chemical equilibria are considered. The two main techniques are Widom's test particle method<sup>5</sup> and grand canonical Monte Carlo simulations (GCMC).<sup>6</sup> Recently, Panagiotopoulos studied the adsorption of Lennard-Jones fluids in a cylindrical pore, using the Gibbs Ensemble Monte Carlo (GEMC) method.<sup>7</sup> This implementation of the GEMC amounts to a modified GCMC simulation wherein the bulk is simultaneously simulated and allowed to exchange particles with the fluid in the pore. More recently Müller et al.<sup>8</sup> applied the same method to the adsorption of polymer fluids. All of these methods rely upon inserting fictitious or real particles into the system under study. While this process is feasible in dilute fluids, it becomes problematic at high densities. This is due to the large probability of overlap between the inserted particle and the other particles in the system.

Adsorption studies based on particle insertion methods are easiest for a dilute monatomic fluid wherein the interaction potentials are relatively simple, e.g., hard spheres, Lennard-Jones, and primitive model electrolytes. These types of potential models minimize the overlap problem. If the fluid was instead to consist of more complex particles, like molecules or polymers, problems would arise at even lower densities. For example, the study by Müller et al. was restricted to tetramers at low densities. The performance of particle insertion methods can be improved by the use of umbrella sampling or biasing techniques that locate "holes" in the fluid.<sup>9,10</sup> However, these methods would still be of limited use in the study of large molecules at high densities. It is thus desirable to develop noninsertion methods which are not so hampered at high density.

Very recently we developed the free energy difference method (FEDM),<sup>11</sup> to simulate confined fluids at constant chemical potential. The technique was illustrated using a repulsive fluid in a planar slit with attractive walls. Simulations were performed in an isobaric ensemble wherein the average of the pressure tensor acting in the direction parallel to the walls,  $P_t$ , was fixed, and the area of the walls was allowed to fluctuate. The FEDM was used to predict accurately the value of  $P_t$  necessary to maintain the fluid at a constant chemical potential, given changes in the separation between the confining walls. Although the simulations were at constant chemical potential, neither the chemical potential nor the density of the bulk were known. One straightforward way to obtain the bulk density would be to separate the walls to

a distance sufficient for the fluid to assume the bulk density at the midplane. In this work, we suggest a more practical alternative. The chemical equilibrium between the confined and bulk systems is first located at low density, where either Widom's method or GCMC simulations are still very reliable. The chemical potential is then increased by the same amount in both systems in a stepwise manner, by changing their respective pressures. This process maintains the systems at equilibrium at each step. In this article we will illustrate this technique for the monatomic repulsive fluid model described above. We chose this system, not only for reasons of simplicity, but also because particle insertion methods can still be relied upon to give reasonable results, even at high densities. This means that Widom's method can be used to independently check our results over a large range of densities. This would not have been possible in the case of a fluid of long flexible molecules or polymers. However, it is precisely for these types of complex fluids with which we hope our method will display its greatest advantage.

## Theory and Simulations

We begin by deriving the FEDM in an isobaric ensemble. Although it is possible to use other ensembles, this choice gives particularly simple expressions. In the case of a planar slit, the independent variables in this ensemble are: the number of particles,  $N$ ; the temperature,  $T$ ; the average pressure tensor acting in the direction parallel to the walls,  $P_t$ ; and the wall separation,  $h$ . The Gibbs free energy,  $G$ , is the natural thermodynamic potential for this ensemble. It is related to the partition function,  $Q$ , according to

$$G = -k_B T \ln Q(N, T, P_t, h) \quad (1)$$

where the partition function is given by

$$Q(N, T, P_t, h) = Q^{(t)} Q^{(c)}(P_t) \quad (2)$$

$Q^{(t)}$  is the momentum contribution and  $Q^{(c)}(P_t)$  is the configurational part, given by

$$Q^{(c)}(P_t) = 1/N! \int_0^\infty h dS \int d\mathbf{r}_1 \dots d\mathbf{r}_N \times \exp(-\beta(U + P_t h S)) \quad (3)$$

$S$  is the area of the walls, with  $U$  the configurational energy, which is a function of the set of

coordinates  $\{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ . The quantity  $\beta = 1/k_B T$ , with  $k_B$  Boltzmann's constant. As the Gibbs free energy is an extensive function of  $N$ , we note that

$$G = N\mu \quad (4)$$

where  $\mu$  is the chemical potential. We now consider changing  $P_t$  by  $\Delta P_t$  at a constant wall separation and temperature. This must cause a change in the chemical potential,  $\Delta\mu$ . Using the above, we get

$$\exp[-N\beta\Delta\mu] = Q^{(c)}(P_t + \Delta P_t)/Q^{(c)}(P_t) \quad (5)$$

and eq. (5) can be rewritten as

$$\exp[-N\beta\Delta\mu] = \int_0^\infty dS f(S, P_t) \exp(-\beta\Delta P_t S h) \quad (6)$$

where  $f(S, P_t)$  is the wall area probability density at  $P_t$ , given by

$$f(S, P_t) = \frac{\int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp(-\beta(U + P_t h S))}{\int_0^\infty dS \int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp(-\beta(U + P_t h S))} \quad (7)$$

In our implementation of the FEDM, the function  $f(S, P_t)$  was obtained from a simulation with the pressure at  $P_t$ . A given  $\Delta\mu$  was then chosen. Using eq. (6) and a suitable numerical root-finding procedure (we used Newton-Raphson),  $\Delta P_t$  at the new chemical potential was then obtained. This procedure was found to be numerically very stable and easily automated to cover a range of chemical potentials in a stepwise fashion. The bulk system was treated in similar fashion. In that case, one has a relation similar to eq. (6), the difference being that the bulk pressure enters and the integration is over the volume, rather than the area, probability density. Thus, starting at a low density, where particle insertion methods can be easily used to locate the equilibrium, one can use eq. (6) to increase the chemical potential of the fluid by the same amount in both systems, ensuring that there is equilibrium at every step.

By expanding the left- and right-hand sides of eq. (5) to first order one obtains a Gibbs-Duhem like relation, namely

$$\frac{d\mu}{dP_t} = \frac{\langle S \rangle h}{N} \quad (8)$$

This corresponds to a first order approximation to

the full FEDM. One could, for example, use it to obtain the first guess for the iterative solution of eq. (5). Integration of the bulk fluid form of eq. (8) was used by Kofke to study gas-liquid coexistence.<sup>12</sup>

For the FEDM to work well, it is necessary that the area (or volume) distribution function sampled at the current step overlaps sufficiently with the one at the next step. This can be achieved by letting the step size be small enough. As eq. (6) is exact for any step size, another alternative, not pursued here, is to use umbrella sampling to widen the simulated distribution.

We illustrate the methodology using a simple fluid model with a pair interaction, given by

$$u(r) = 4\epsilon \left( \frac{\sigma}{r} \right)^{12} \quad (9)$$

where  $r$  is the separation, and  $\epsilon$  and  $\sigma$  are the energy and size parameters, respectively. This potential is sufficiently short ranged so as not to manifest significant finite volume effects. The confined fluid interacts with two infinite planar Lennard-Jones walls, located at  $z = 0$  and  $z = h$ . The interaction with the walls is:

$$V(z) = w(z) + w(h - z) \quad (10)$$

where

$$w(z) = 2\pi\sigma^3\epsilon n_w \left( \frac{2}{45}(\sigma/z)^9 - \frac{1}{3}(\sigma/z)^3 \right) \quad (11)$$

and  $n_w$  is the density of particles in the walls. The parameters were chosen to be consistent with our previous simulations<sup>11</sup>; i.e.,  $\epsilon/k_B = 200$  K,  $\sigma = 3$  Å,  $n_w\sigma^3 = 1.00$ , and  $T = 298$  K. The Metropolis algorithm,<sup>9,11</sup> was used both to displace particles and to vary the box dimensions. For the nonuniform system, changes in the wall area were attempted with probability  $1/N$ . As volume changes in the bulk system are computationally cheaper, these were attempted considerably more often. Both the particle displacements as well as the volume changes were adjusted to give an acceptance probability of 50%.

## Results and Discussion

### PORE-BULK EQUILIBRIUM

A pressure of  $10^8$  Pa in the bulk was low enough to allow the accurate location of chemical equilibrium with the fluid in the pore, using

Widom's particle insertion method. This was done for a system with 64 particles. We used  $3 \times 10^3$  configurations for equilibration and  $4 \times 10^5$  configurations per particle for production. Test particle insertions were attempted one tenth as often as particle displacements. The excess chemical potential (beyond the ideal gas),  $\mu^{ex}$ , was found to be  $2.604 \pm 0.003$  (in units of  $k_B T$ ). The uncertainty was obtained as the standard error of the mean of 10 subaverages. Each subaverage was thus obtained over  $4 \times 10^4$  configurations per particle. This is many times longer than the number of correlated Monte Carlo steps typical for this fluid. Some time ago, Adams<sup>13</sup> used Widom's method to study chemical potentials in hard sphere fluids. The number of attempted insertions of test particles in this work is several times more than that used by Adams at a comparable density.

Two different wall separations were investigated,  $h = 10 \text{ \AA}$  and  $16 \text{ \AA}$ . The pressures,  $P_i$ , needed to obtain chemical equilibrium with the bulk at these separations, were estimated with a few simulations for each separation. They were  $1.066 \times 10^8 \text{ Pa}$  and  $1.043 \times 10^8 \text{ Pa}$  for  $10 \text{ \AA}$  and  $16 \text{ \AA}$ , respectively. The uncertainty in these numbers was  $2 \times 10^5 \text{ Pa}$ . The chemical potential was then incrementally changed by the same amount in both the bulk and the slits, using a constant step size. In total, the chemical potential was increased by  $8 k_B T$ . Once the highest chemical potential was reached, we checked for hysteresis by taking steps (of the same size) in the reverse direction and returned to what should have been the initial state. Any deviation between the starting and final pressures was an indication of whether the step size was sufficiently small.

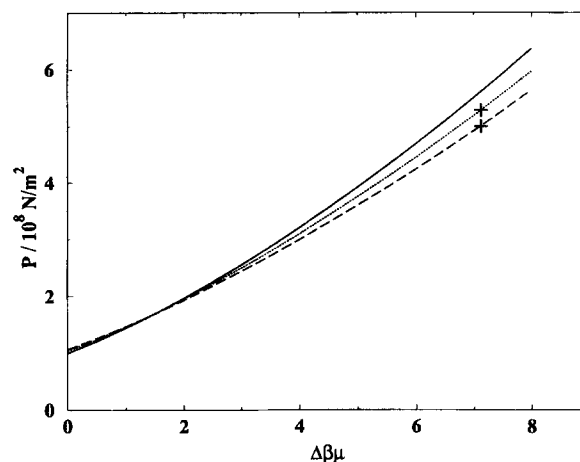
We investigated step size dependence using three different series of simulations with different step sizes for the chemical potential. The steps were 0.5, 1.0, and 2.0 (in units of  $k_B T$ ). We used 64 particles with 3000 configurations per particle for equilibrations at each step. For production, each of the series used a total of  $4.8 \times 10^5$  displacements per particle for the combined forward and return journeys in chemical potential space. That is, neglecting equilibrations at each step, all of the simulations required the same computational effort. Only the results for the bulk fluid are reported here. The fluid in the pore behaved similarly.

For the smallest step size, 0.5, the bulk pressure at the maximum chemical potential was  $6.361 \times 10^8 \text{ Pa}$ . Upon checking for hysteresis, we found the difference between the initial bulk pressure ( $10^8 \text{ Pa}$ ) and that obtained returning was only  $10^5 \text{ Pa}$ .

For the 1.0 step this difference was approximately  $5 \times 10^5 \text{ Pa}$ , and for the 2.0 step it was approximately  $7 \times 10^6 \text{ Pa}$ . A  $10^5\text{-Pa}$  discrepancy in the pressure at the low density point corresponded to an error in the chemical potential of only 0.003, which was of the same order as the uncertainty obtained from Widom's method. Given that this error in the pressure is the result of accumulated errors at the other (higher) pressures, the actual uncertainty in the chemical potential, due to step size at any particular density, should be considerably smaller than 0.003. Thus, we were satisfied that a step size of 0.5 gave sufficient accuracy, and all subsequent calculations used this value.

Given the short range of the pair potential, finite volume effects were not expected to be large. We checked this by performing bulk fluid simulations with 128 particles. The difference in the pressure between the 128 and 64 particle simulations, at the maximum chemical potential, was only  $4 \times 10^5 \text{ Pa}$ . Again, this was quite small in comparison to the total pressure.

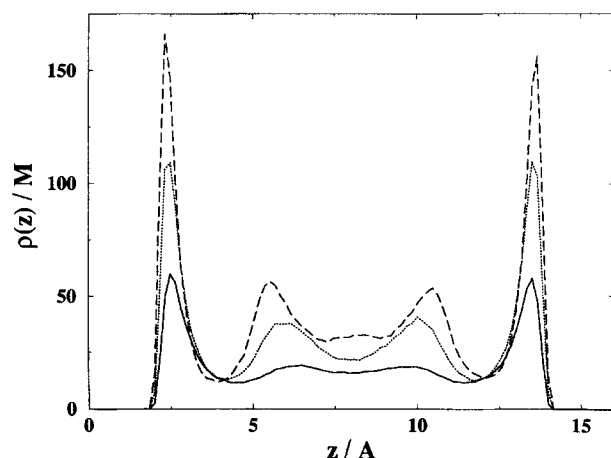
Figure 1 shows how the bulk and pore pressures vary with the chemical potential. At the lowest chemical potential, the pressure in the slit is generally lower than in the bulk. This is due to the presence of the attractive wall-fluid potential, which decreases the chemical potential in the slit. To maintain equilibrium with the bulk, the pres-



**FIGURE 1.** The bulk and the slit pressure as a function of the chemical potential of the fluid. At the lowest chemical potential,  $\beta \Delta \mu = 0$ , the bulk pressure is  $10^8 \text{ Pa}$  and the equilibria is located using the test particle method. The rest of the results are generated with the FEDM, with a step size of  $0.5 k_B T$ . (—) bulk, (···)  $h = 16 \text{ \AA}$ , (--)  $h = 10 \text{ \AA}$  and (+) are results obtained from ref. 11 (see text).

sure in the slit must then be higher, thus reducing the free volume of particles. At higher chemical potential, and hence bulk density, we begin to observe significant structuring of the fluid in the slit (see Fig. 2). In the more structured fluid,  $P_t$  is required to be *lower* than the bulk pressure to maintain equilibrium. This is probably due to the difficulty of packing repulsive particles in narrow pores at high density. The corresponding reduction in entropy counteracts the energetic advantage of the attractive wall interaction. Figure 1 also includes two points from a previous FEDM study<sup>11</sup> wherein the wall separation was varied at constant chemical potential. In that work, it was predicted that, at a separation of  $h = 10 \text{ \AA}$ , the chemical potential at  $P_t = 5.000 \times 10^8 \text{ Pa}$  was equal to that of the system at  $h = 16 \text{ \AA}$ , with  $P_t = 5.279 \times 10^8 \text{ Pa}$ . These pressures fall nicely on the curves in Figure 1 and provide independent confirmation of the accuracy of the present simulations.

As a further check of our technique, the excess chemical potential was also estimated with Widom's test particle method at each step. The procedure used was as described above. Though the test particle results were less accurate, they did agree with the FEDM results. For example, at the highest pressure, the excess chemical potential obtained with Widom's method was  $\beta\mu^{ex} \approx 9.9 \pm 0.1$ . Knowing the excess chemical potential at the starting density, we obtained, from the FEDM calculation,  $9.821 \pm 0.005$  and  $9.829 \pm 0.005$  for 64 and 128 particles, respectively. The quoted statistical errors were estimated from the uncertainty in the chemical potential of the initial system, as well



**FIGURE 2.** The molar concentration of particles in a slit with  $h = 16 \text{ \AA}$ , at different chemical potentials of the fluid. (—)  $\beta\Delta\mu = 0$ , (···)  $\beta\Delta\mu = 4$ , and (---)  $\beta\Delta\mu = 8$ .

as the observed hysteresis effects. The FEDM results are very accurate, compared with the Widom estimate. One could argue that the accuracy of the FEDM chemical potentials was obtained at the expense of a passage over intermediate chemical potential states. Often, however, these intermediate states are of interest. In this case, for example, they can be used to construct the adsorption isotherm in the slit as a function of the chemical potential, or equivalently, the bulk density.

## DENSE BULK FLUID

To check the limits of the FEDM, further series of simulations were performed on the bulk fluid only, which increased the chemical potential in steps of  $0.5 k_B T$  from  $\beta\Delta\mu = 8$  to 12. The pressure for  $\beta\Delta\mu = 12$  was  $1.0195 \times 10^9 \text{ Pa}$  and the observed hysteresis in the pressure, upon returning to the state at  $\beta\Delta\mu = 8$ , was only  $10^5 \text{ Pa}$ . The small hysteresis observed in this series of simulations shows that the FEDM is accurate even for these very dense systems. At first thought one would think that, due to the small compressibility of the dense system, overlap of the volume distribution functions at successive steps would be small. However, the smaller compressibility also means that the average volume change between steps is also small and the distribution functions, though narrower, move closer together. Indeed, given that one is sampling over a smaller range in volumes, it is reasonable to expect that the uncertainty in dense systems is smaller than at low density. This conjecture has been confirmed in some test calculations. It is relevant to note, at this point, that the distance between successive volume distribution functions scales as  $N$ , the number of particles (i.e., as the isothermal compressibility), but the width of the distributions scales as  $N^{1/2}$ . Thus, one would require smaller steps given a larger number of particles. The advantages of using smaller numbers of particles to increase fluctuations is typical for free energy methods.

One may expect that finite volume effects could become important at higher densities. For instance, in the bulk fluid, at a pressure of around  $10^9 \text{ Pa}$ , the radial distribution function was strongly oscillating and showed significant structure at the boundaries of the box. To investigate the importance of these effects we again compared simulations of 64 and 128 particles. For the 128-particle simulations, the pressure at  $\beta\Delta\mu = 12$  was only  $4 \times 10^5 \text{ Pa}$  above that of the 64-particle simulation, which is small compared to the total pres-

sure. For this system, Widom's method, with 128 particles, estimated  $\beta\mu^{ex}$  to be  $13.9 \pm 0.3$ , whereas the FEDM gave  $13.665 \pm 0.006$  and  $13.674 \pm 0.006$  for the 64- and 128-particle systems, respectively. The Widom result is less accurate, but is almost significantly higher than the FEDM values. The discrepancies are resolved when we note that longer test particle simulations, using  $4 \times 10^5$  configurations per particle, gave  $\beta\mu^{ex} = 13.68 \pm 0.08$  and  $13.63 \pm 0.07$  for the 64- and 128-particle simulations, respectively. These numbers confirm the FEDM results.

### EXCESS ADSORPTION

Figure 2 shows the concentration profile between the walls, at  $h = 16 \text{ \AA}$ , for varying chemical potential (bulk density). At the lowest chemical potential, the profile shows an adsorption peak, due to the attractive wall interactions, as well as the signs of oscillating structure. As the chemical potential increases, the interparticle repulsions play a larger role and packing effects increase. At the highest chemical potential, the concentration profile shows strong oscillations, typical of dense fluids.

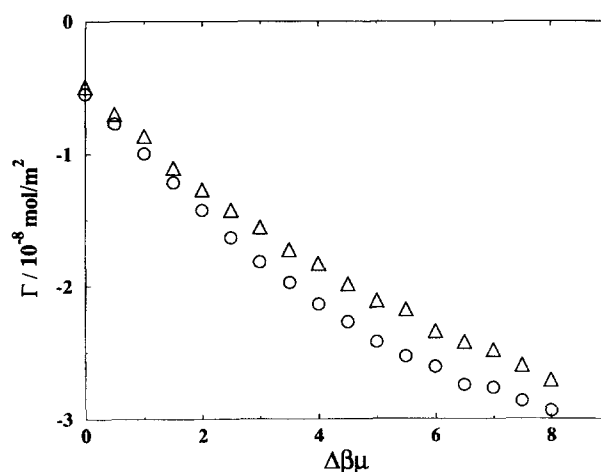
The FEDM, as implemented in this work, is ideally suited to calculate the adsorption isotherms of the confined fluid as a function of the chemical potential. The excess absorption per unit area in the slit,  $\Gamma$ , is given by

$$\Gamma = \frac{1}{2} \int_0^h dz (\rho(z) - \rho) \quad (12)$$

where  $\rho$  is the bulk density. Figure 3 shows how the excess absorption varies with the chemical potential. Given that the walls are attractive, one would expect  $\Gamma$  to be positive. However, the repulsive pair potential and the depletion regions within a distance  $\sigma$  of the walls conspire to make  $\Gamma$  negative for the densities considered here. If the integration limits are taken to be within  $\sigma$  of the walls,  $\Gamma$  is actually positive. One interesting feature is that  $\Gamma$  becomes more negative as the chemical potential increases. This is due to the decreasing importance of the attractive wall potential, and the increasing role played by packing, as the density increases.

### Conclusions

In this work we have implemented a new method for simulating chemical equilibria of con-



**FIGURE 3.** The excess absorption per unit area in the slit as a function of the chemical potential. (○)  $h = 10 \text{ \AA}$  and (Δ)  $h = 16 \text{ \AA}$ .

finer fluids. The accuracy of the method was investigated for a repulsive fluid in a planar slit in equilibrium with a bulk. Equilibrium was established at low density, using Widom's test particle method. The chemical potentials of the confined and bulk systems were then increased by the same amount in a stepwise manner. The lack of significant hysteresis in complete cycles showed that the equilibrium conditions could be accurately determined even at high densities, where particle insertion methods become inefficient. We used Widom's particle insertion method to check our approach. The chemical results were consistent, though the uncertainties in the test particle values were at best some 10 times larger than the FEDM estimates at high density.

The FEDM is very general and may be implemented in a variety of ways. One may, for instance, change the pair interaction or the pore size, while maintaining chemical equilibrium. Furthermore, as no particle exchanges are made, it is admirably suited to the simulation of complex fluids. Preliminary results for soft repulsive polymers have been very successful. One of our aims for future studies is to apply this method to map out adsorption isotherms for polymer solutions. It is our belief that such implementations of the FEDM will be important tools for future studies of equilibria involving complex fluids.

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